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(54) Title: DENTAL COMPOSITES COMPRISING GROUND, DENSIFIED, EMBRITTLED GLASS FIBER FILLER			
(57) Abstract			
<p>A composite for a dental restoration is presented comprising ground, densified, embrittled glass fibers together with fillers and a polymeric matrix precursor composition. The ground, densified, embrittled glass fibers are obtained by grinding glass fibers which have been densified and embrittled by heating glass fibers at a temperature substantially below the softening point of the glass fibers, without significant fusion or melting together of the fibers. The composite is particularly useful as a direct filling material, in that it has the feel and workability of an amalgam.</p>			

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DENTAL COMPOSITES COMPRISING GROUND,
DENSIFIED, EMBRITTLED GLASS FIBER FILLER

Background of the Invention:

1. Field of the Invention

This invention relates to dental composite materials and methods of manufacture thereof. In particular, this invention relates to improved glass fiber fillers for dental composite materials, wherein the glass fibers are densified and embrittled by heating the fibers.

2. Brief Discussion of the Related Art

Compositions useful for repairing damaged teeth in situ are known in the art as direct filling materials, and include alloys and resin composites. Dental amalgam alloys have widely been used as direct filling material, and provide excellent handling characteristics, and physical properties. The technique of mechanically packing and condensing a material into a tooth cavity is previously known to the dental profession in connection with the use of dental amalgams as a direct filling material. It has well known advantages in that it permits a close adaptation of the filling material to the cavity walls and also makes it possible to make firm contacts between the restored

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tooth and its neighbor. Further, it makes it possible to give the restoration its final anatomic form before hardening, thereby avoiding the time consuming and difficult finishing work with rotating instruments required with composite materials. These advantages are achieved by the densified, embrittled glass fiber composites on the present invention and the method of manufacture thereof. However, there are perceived health hazard concerns regarding the use of high amounts of mercury or gallium present in amalgam alloys.

Dental resins have accordingly been developed, which comprise polymeric matrices, for example polyamides, polyesters, acrylates, polyolefins, polyimides, polyarylates, polyurethanes, vinyl esters, or epoxy-based materials. Other polymeric matrices include styrenes, styrene acrylonitriles, ABS polymers, polysulfones, polyacetals, polycarbonates, polyphenylene sulfides, and the like. The most popular polymeric matrices are based on monomers having at least one ethylenically unsaturated group, in particular acrylate and methacrylate groups. One commonly used monomer of this class is the reaction product of bisphenol A with glycidyl methacrylate (hereinafter BIS-GMA). In addition, these resins have also been used to make artificial teeth and denture bases.

Unfilled (i.e., pure) curable acrylic and methacrylic resins generally suffer from polymerization shrinkage and poor durability. These drawbacks have been reduced in direct filling applications, in part, through the addition of inert fillers. See, for example, U.S. Patent No. 3,066,112 which is herein incorporated by reference. The combination of binder plus filler is commonly referred to as a composite direct filling material. Currently used fillers for curable dental resins generally are inert materials in the form of finely divided irregular particles, fibers or beads, present in an amount from about 35 to about 80 percent by weight of the total composite direct filling material.

Commonly used inorganic fillers include fused silica, quartz, glass, various mineral silicates (e.g., β -eucryptite, lepidolite, petalite, sponcumene, beryl, topaz and zircon), silicon carbide, alumina, and mixtures thereof. Commonly-assigned U.S. Patent No. 4,544,359 to Waknine, for example, discloses a filler mixture comprising barium silicate, borosilicate glass, and colloidal silica. In general composite direct

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filling materials which are fully loaded with inorganic fillers (i.e. combined with the highest workable volume loading) having particles in the range of 0.01 - 1.2 microns are the most wear-resistant currently available composite direct filling materials. However, these composite direct filling materials containing finely divided inorganic fillers and acrylic binder resins may not polish as easily as unfilled dental resin.

Organic materials have also been used as fillers. For example, U.S. Patent No. 3,923,740 discloses a direct filling material containing finely divided cured polymethyl methacrylate, alone or in conjunction with an inorganic filler. Composite direct filling materials which are wholly or partly filled with finely divided polymethyl methacrylate have better polishability (i.e. better surface finish after polishing with ordinary dental tools) than composite direct filling materials which are fully loaded with inorganic fillers, but generally have poorer durability (i.e. poorer wear resistance in vivo) than composite direct filling materials having inorganic fillers only.

Regarding fibrous fillers in particular, U.S. Patent No. 2,477,268 to Saffir discloses short glass fibers randomly dispersed in dental resin materials, as does U.S. Patent No. 2,514,076 to Kelly. Use of long, fully wetted fibers in structural components for dental restorations and the like are disclosed in U.S. Patent Nos. 4,894,102 to Goldberg et al. However, none of these patents discloses a composite having the feel of amalgam.

Fused-fibrous filler compositions in the dental arts are also known. Such fused fibrous fillers are of particular interest because they reportedly provide a feel similar to that of amalgam when used by the dentist, and may be applied using similar techniques. In U.S. Patent No. 4,381,918 and No. 4,392,828 to Ehrnford there is disclosed a filler comprising porous inorganic particles which are completely or partially impregnated with a resin material. The porous inorganic particles are formed by heating inorganic fibers under pressure to fuse the fibers at their points of contact, thereby forming a rigid three-dimensional network of inorganic fibers. Fused-fibrous filler compositions are also disclosed in U.S. Patent No. 5,621,035 to Lyles et al. Such fillers comprise silica fibers together with either alumina or aluminosilicate fibers which are fused in the presence of a fusion source such as boron nitride. The presence of boron lowers the

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melting point of the fibers sufficiently to allow formation of a porous, interconnected network. The network is then ground to particles having a size of about 180 microns, and used as fillers in dental composites.

5 Unfortunately, use of the fused-fibrous filler compositions disclosed in the Ehrnford and Lyles patents requires multiple steps and extensive preparation time. Accordingly, there is a need in the dental arts to develop a dental resin composite which is similar to or approaching to dental amalgam alloys in handling characteristics, physical properties, and applications without the drawbacks and deficiencies associated with dental amalgam alloys, and without the multiple preparation steps required for
10 fused-fibrous compositions.

Summary of the Invention:

The above-described and other problems and deficiencies of the prior art are overcome or alleviated by the composition and method of manufacture of the present invention, comprising ground, densified, embrittled glass fiber fillers and a polymeric
15 matrix. In accordance with the present invention, glass fibers are densified and embrittled by heating the glass fibers at an effective temperature substantially below the softening point of the glass fibers such that the glass fibers are densified and embrittled, which as used herein excludes fusing or melting together. The densified, embrittled fibers are then ground to a fibrous particle size preferably less than about 80 microns
20 (μm). The ground, densified, embrittled glass fibers of the present invention are preferably used as a filler component of a dental composite, being present in the range from about 5 % to about 95 % by weight of the total composition, depending upon the use made of the polymerized composition. In addition to the ground, densified, embrittled glass fibers, the polymeric matrix may further comprise other fillers known
25 in the art.

The resulting dental composite exhibits handling characteristics similar to or approaching that of dental amalgam, and is particularly a suitable substitute filling for amalgam without the alleged health hazard concerns. The physical properties of the dental composite of the present invention include a modulus of elasticity of greater than

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approximately 15 GPa and modulus range between approximately 15 and approximately 22 GPa which is much higher than conventional dental composites which possess an elastic modulus of approximately 10 GPa. The elastic modulus of the composite of the present invention is comparable to amalgam which exhibits an elastic modulus of approximately 20 GPa. A relatively low modulus may cause a temporary displacement of the restoration resulting from normal masticatory stresses. Eventually this may cause leakage that may lead to secondary caries. Such movement or displacement is less likely to occur with materials having a high elastic modulus such as the composite of the present invention. Further, the composite exhibits a Vicker's hardness of approximately 1,250 MPa enabling it to withstand stress better than conventional dental composites having a hardness in the range of 600 to 700 MPa. The wear rate is very low, averaging about 3.5 microns per year which is comparable to that exhibited by amalgam. The water sorption of the composite of the present invention is approximately 8.9 $\mu\text{g}/\text{mm}/\text{week}$ and polymerization shrinkage by volume is approximately 1.98%. The depth of cure of the composite is at least 5 mm which allows for bulk-fill application which is partly a result of the glass fibers used in the filler component. The fibers serve as transparent pipes which transmit light to the bottom of the restoration. The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings.

Brief Description of the Drawings:

For the purpose of illustrating the invention, there are shown in the drawing forms which are presently preferred; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities shown. Referring now to the drawings wherein like elements are numbered alike in the several FIGURES:

FIGURE 1 is a photomicrograph of glass fibers before heating the glass fibers in accordance with the present invention.

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FIGURE 2 is a photomicrograph of the densified, embrittled glass fibers after the glass fibers have been heated substantially below the softening point of the glass fibers.

FIGURES 3A and 3B are photomicrographs at an (A) 10 micron and (B) 100 micron scale of the densified, embrittled glass fibers after grinding to a particle size of less than about 80 μm .

Detailed Description of the Invention:

The present invention is a dental restoration material comprising a polymeric matrix and ground, densified, embrittled glass fibers, wherein the glass fibers have been densified and embrittled by heating the glass fibers at a temperature substantially below the softening point of the glass fibers. Glass fibers as ordinarily provided by the manufacturer tend to be less dense, and somewhat flexible, that is, capable of being bent without breaking. As used herein, the term "densify" means to cause the fibers to become more dense, that is, to shrink in volume with practically no fusing or melting together of the fibers at their points of contact. "Embrittled" as used herein means to cause the fibers to become more prone to breakage upon the application of force, with practically no fusing or melting together of the fibers at their points of contact. Further as used herein, the term "substantially below" refers to a temperature effective to densify and embrittle the glass fibers, but not to fuse or melt the glass fibers together at their points of contact. The densified, embrittled glass particles are then cooled and ground to a particle size less than about 80 microns according to grinding methods known in the art.

A number of glass compositions are suitable for use in the practice of the present invention, including but being limited to known glasses listed in the Table below. A preferred glass composition is fibers comprising S-2 GLASS[®], which is commercially available from Owens Corning. Such fibers have diameters of about 10 microns.

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	Oxide*	A-Glass	C-Glass	D-Glass	E-Glass	ECR-Glass®	AR-Glass	R-Glass	S-2 Glass®
	SiO ₂	63-72	64-68	72-75	52-56	54-62	55-75	55-65	64-66
	Al ₂ O ₃	0-6	3-5	0-1	12-16	9-15	0-5	15-30	24-25
	B ₂ O ₃	0-6	4-6	21-24	5-10		0-8		
5	CaO	6-10	11-15	0-1	16-25	17-25	1-10	9-25	0-0.1
	MgO	0-4	2-4		0-5	0-4		3-8	9.5-10
	ZnO					2-5			
	BaO		0-1						
	Li ₂ O						0-1.5		
10	Na ₂ O + K ₂ O	14-16	7-10	0-4	0-2	0-2	11-21	0-1	0-0.2
	TiO ₂	0-0.6			0-1.5	0-4	0-12		
	ZrO ₂						1-18		
	Fe ₂ O ₃	0-0.5	0-0.8	0-0.3	0-0.8	0-0.8	0-5		0-0.1
15	F ₂	0-0.4			0-1		0-5	0-0.3	
	Softening point, °C	705	750	771	846	882	773	952	1056

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*Percent by weight

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In the practice of the present invention, glass fibers are densified and embrittled by heating at a temperature substantially below the softening point of the glass for a time effective to densify the glass. Such temperature and time are interdependent, and are empirically determined, based on the composition (and thus the softening point) of the glass. Higher temperatures will generally result in shorter times. The temperature must be high enough to effect densification and embrittlement, but not so high as to cause fusion, while the time of heating must be such as to allow even heating, but again, no fusion of the fibers at the chosen temperature.

In a preferred embodiment, at atmospheric pressure, the temperature is at least about 75 °C below the softening point of the glass, and more preferably, at atmospheric pressure, the temperature is between about 100 °C and about 140 °C below the softening point of the glass. S-2 GLASS®, for example, has a softening point of 1056 °C. In accordance with the present invention, the S-2 GLASS® fibers are preferably heated at a temperature between about 920 °C to about 950 °C for about 0.5 to 4 hours, a time period effective to densify the glass fibers but not fuse or melt the glass fibers together. In a particularly preferred embodiment, the S-2 GLASS® fibers are heated at a temperature of about 940 °C for about 2 hours.

After densification, the glass fibers are ground to a size suitable for use as a filler in a dental restoration, preferably below about 100 microns. As used herein, grinding refers to any known methods for size reduction, including reduction to spherical or fiber form. To obtain the desired amalgam "feel", the particles are ground to a size of less than about 80 microns. At this size, the particles generally retain a fibrous form, that is, a length greater than their diameter.

The polymeric matrix portion of the dental composite is selected from those known in the art of dental materials, including but not being limited to expandable monomers, liquid crystal monomers, ring-opening monomers, polyamides, acrylates, polyesters, polyolefins, polyimides, polyarylates, polyurethanes, vinyl esters or epoxy-based materials. Other polymeric matrices include styrenes, styrene acrylonitriles, ABS polymers, polysulfones, polyacetals, polycarbonates, polyphenylene sulfides, and the like. These polymeric matrices are derived from curing polymeric

matrix precursor compositions. Such precursor compositions are well-known in the art, and may be formulated as one-part, two-part, or other compositions, depending on the components.

Preferred materials include those based on acrylic and methacrylic monomers, for example those disclosed in U.S. Pat. No. 3,066,112, No. 3,179,623, and No. 3,194,784 to Bowen; U.S. Patent No. 3,751,399 and No. 3,926,906 to Lee et al.; and commonly assigned U.S. Pat. No. 5,276,068 to Waknine and Application Serial No. 60/036,184 filed on January 17, 1997, all of which are herein incorporated by reference in their entirety. Especially preferred methacrylate monomers include the condensation product of bisphenol A and glycidyl methacrylate, 2,2'-bis [4-(3-methacryloxy-2-hydroxy propoxy)-phenyl] propane (hereinafter abbreviated BIS-GMA), the condensation product of ethoxylated bisphenol A and glycidyl methacrylate, (hereinafter EBPA-DMA), and the condensation product of 2 parts hydroxymethylmethacrylate and 1 part triethylene glycol bis(chloroformate) (hereinafter PCDMA). Polyurethane dimethacrylates (hereinafter abbreviated to PUDMA) are also commonly-used principal polymers suitable for use in the present invention.

The polymeric matrix precursor composition may further comprise a co-polymerizable diluent monomer. Such monomers are generally used to adjust the viscosity of the polymerizable composition, which affects wettability of the composition. Suitable diluent monomers include, without limitation, hydroxyalkyl methacrylates, such as 2-hydroxyethyl methacrylate, 1,6-hexanediol dimethacrylate, and 2-hydroxypropyl methacrylate; glyceryl dimethacrylate; ethyleneglycol methacrylates, including ethyleneglycol methacrylate, diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate and tetraethyleneglycol dimethacrylate; or diisocyanates, such as 1,6-hexamethylene diisocyanate. Triethyleneglycol dimethacrylate (TEGDMA) is particularly preferred for use in the present invention.

The polymeric matrix precursor composition typically includes polymerization initiators, polymerization accelerators, ultra-violet light absorbers, anti-oxidants, fluorescent whitening agents, and other additives well known in the art. The polymer

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matrices may be visible light curing, self-curing, dual curing, and vacuum-, heat-, and pressure-curable compositions as well as any combination thereof. Visible light curable compositions employ light-sensitive compounds such as benzil diketones, and in particular, dl-camphorquinone in amounts ranging from about 0.05 to 0.5 weight percent. UV absorbers are particularly desirable in the visible light curable compositions in order to avoid discoloration of the resin from any incident ultraviolet light. Suitable UV absorbers are the various benzophenones, particularly UV-9 and UV-5411 available from American Cyanamid Company, and benzotriazoles known in the art, particularly 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, sold under the trademark TINUVIN P by Ciba-Geigy Corporation, Ardsley, N.Y. in amounts ranging from about 0.05 to about 5.0 weight percent.

In the self curing compositions, a polymerization accelerator may be included in the polymerizable monomer composition. The polymerization accelerators suitable for use include the various organic tertiary amines well known in the art, generally aromatic tertiary amines, such as dimethyl-p-toluidine, dihydroxyethyl-p-toluidine and the like, in amounts ranging from about 0.05 to about 4.0 weight percent, and generally acrylate derivatives such as dimethylaminoethyl methacrylate and particularly, diethylaminoethyl methacrylate in amounts ranging from about 0.05 to 0.5 weight percent.

The heat and pressure curable compositions include, in addition to the monomeric components, a heat cure initiator such as benzoyl peroxide, 1,1'-azobis(cyclohexanecarbonitrile), or other suitable free radical initiators. Particularly suitable free radical initiators are lauroyl peroxide, tributyl hydroperoxide, AIBN and, more particularly benzoyl peroxide or 1,1'-azobis(cyclohexanecarbonitrile).

The total amount of filler is determined by the specific function of the filled materials, being in the range from about 5 to 95% by weight of the total composite composition. Preferably, the composites of the present invention may also include other inorganic and/or organic fillers or a mixtures thereof currently used in dental restorative materials. When used as a direct filling material, the desired amalgam "feel" is obtained by using about 10 to about 60 % by weight of ground, densified,

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embrittled glass fiber and from about 30 to about 80 % by weight of other filler, for example barium borosilicate. A preferred composition comprises about 15 % by weight of a resin mixture comprising EBPA-DMA and PCDMA in a ratio of 70:30 by weight, about 35% by weight of ground, densified, embrittled glass filler, and about 50 % by weight of barium borosilicate filler.

Examples of other suitable filling materials include, but are not limited to, silica, silicate glass, quartz, barium silicate, strontium silicate, barium borosilicate, strontium borosilicate, borosilicate, lithium silicate, amorphous silica, ammoniated or deammoniated calcium phosphate and alumina, zirconia, tin oxide and titania. Suitable fillers for dental filling-type materials prepared in accordance with this invention are those having a particle size ranging from about 0.1-5.0 μ m with a silicate colloid of 0.001 to about 0.07 microns and prepared by a series of milling steps comprising wet milling in an aqueous medium, surface etch milling and silanizing milling in a silane solution. Some of the aforementioned inorganic filling materials are disclosed in U.S. Pat. No. 4,544,359 and No. 4,547,531, pertinent portions of which are incorporated herein by reference.

Referring now to the drawings wherein like numerals indicate like elements, FIGURE 1 is a photomicrograph of S-2[®] glass fibers 10 before the fibers have been densified and embrittled. FIGURE 2 illustrates S-2[®] glass fibers 12 which have been densified and embrittled by heating the glass fibers at a temperature substantially below the softening point of the glass fibers in accordance with the present invention. The glass fibers 12 are not fused or melted. FIGURES 3A and 3B are photomicrographs illustrating the densified, embrittled glass fibers 14 of the present invention after grinding.

The dental composites of the present invention provide improved handling characteristics, physical properties, and provide an attractive substitute to dental amalgam alloys as direct filling materials. The physical properties include a modulus of elasticity of greater than approximately 15 and approximately 22 GPa which is much higher than conventional dental composites which possess an elastic modulus of approximately 10GPa. The elastic modulus of the composite of the present invention is

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comparable to amalgam which exhibits an elastic modulus of approximately 20 GPa. A relatively low modulus may cause a temporary displacement of the restoration resulting from normal masticatory stresses. Eventually this may cause leakage that may lead to secondary caries. Such movement or displacement is less likely to occur with materials having a high elastic modulus such as the composite of the present invention. Further, the composite exhibits a Vicker's hardness of approximately 1,250 MPa enabling it to withstand stress better than conventional dental composites having a hardness in the range of 600 to 700 MPa. The wear rate is very low, averaging about 3.5 microns per year which is comparable to that exhibited by amalgam. The water sorption of the composite of the present invention is approximately $8.9 \mu\text{g}/\text{mm}^3/\text{week}$ and polymerization shrinkage by volume is approximately 1.98% The depth of cure of the composite is at least 5 mm which allows for bulk-fill application which is partly a result of the glass fibers used in the filler component. The fibers serve as transparent pipes which transmit light to the bottom of the restoration. The composites allow use of mechanical packing and condensing with its attendant advantages. The ground, densified, embrittled glass fiber filler of the present invention may further be utilized in numerous other applications in the practice of dentistry, including periodontal splitting, tooth replacement, tooth stabilization, bridge manufacture, and the like. All of these will not be described herein, as such dental operations are well known to those practicing dentistry, i.e. those of ordinary skill in the art.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

What is claimed is:

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CLAIM 1. A method of making a composition for forming a dental composite material, comprising

heating glass fibers at a temperature of at least 75 °C below the softening point of the glass fibers for a period of time effective to densify the glass fibers;

5 cooling the densified, embrittled glass fibers;

grinding the densified, embrittled glass fibers to form ground, densified, embrittled glass particles; and

incorporating the ground, densified, embrittled glass particles into a polymeric matrix precursor composition to form a dental composite material.

CLAIM 2. The method of claim 1, wherein the heating temperature is between 100 °C and 140 °C below the softening point of the glass.

CLAIM 3. The method of claim 1 or 2, wherein the glass particles have a composition comprising about 64-66 % SiO₂, 24-25 % Al₂O₃, 0-0.1 % CaO, 9.5-10 % MgO, 0-0.2% Na₂O + K₂O, and 0-0.1% Fe₂O₃.

CLAIM 4. The method of claim 1-3, wherein the temperature is in the range between 920 °C and 950 °C.

CLAIM 5. The method of claim 1-4 wherein the ground, densified, embrittled glass particles have an average particle size of less than 80 microns.

CLAIM 6. The method of claim 1-5, wherein the ground, densified, embrittled glass particles comprise from 5 % to 80 % by weight of the total dental composite material.

CLAIM 7. The method of claim 1-6, wherein the dental composite material is cured to yield a material having an elastic modulus of greater than 15 GPa after cure.

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CLAIM 8. The method of claim 1-7, wherein the elastic modulus is between 15 GPa and 22 GPa.

CLAIM 9. The method of claim 1-8, wherein the dental composite material is cured to yield a material having a Vicker's hardness of 1250 MPA after cure.

CLAIM 10. The method of claim 1-9, wherein the dental composite material is cured to yield a material having a water sorption of $8.9 \mu\text{g}/\text{mm}^3/\text{week}$ after cure.

CLAIM 11. The method of claim 1-10, wherein the dental composite material is cured to yield a material having a depth of cure of at least 5 mm after cure.

CLAIM 12. A dental composite composition for forming a dental restoration comprising

ground, densified, embrittled glass particles; and
a polymeric matrix precursor composition.

CLAIM 13. The composite of claim 12, wherein

the glass particles have a composition comprising about 64-66 % SiO_2 , 24-25 % Al_2O_3 , 0-0.1 % CaO , 9.5-10 % MgO , 0-0.2% $\text{Na}_2\text{O} + \text{K}_2\text{O}$, and 0-0.1% Fe_2O_3 .

CLAIM 14. The composite of claim 12 or 13, wherein

the ground, densified, embrittled glass particles have an average particle size of less than about 80 microns.

CLAIM 15. The composite of claim 12-14, wherein the polymeric matrix precursor composition comprises at least one acrylate or methacrylate monomer.

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CLAIM 16. The composite of claim 12-15, wherein the ground, densified, embrittled glass particles comprise from about 5% to about 80% by weight of the total composite composition.

CLAIM 17. The composite of claim 12-16, wherein the ground, densified, embrittled glass particles comprise about 35% by weight of the total composite composition.

CLAIM 18. The composite of claim 12-18, wherein the dental composite comprises at least one additional filler material, wherein the filler material is at least one of silica, silicate glass, quartz, barium silicate, strontium silicate, barium borosilicate, borosilicate, lithium silicate, amorphous silica, ammoniated or deammoniated calcium phosphate, alumina, zirconia, tin oxide or titania.

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CLAIM 19. A dental restoration comprising
ground, densified, embrittled glass particles; and
a cured polymeric matrix composition.

CLAIM 20. The dental restoration of claim 19, wherein
the glass particles have a composition comprising about 64-66% SiO_2 , 24-25% Al_2O_3 , 0-0.1% CaO , 9.5-10% MgO , 0-0.2% $\text{Na}_2\text{O} + \text{K}_2\text{O}$, and 0-0.1% Fe_2O_3 .

CLAIM 21. The dental restoration of claim 19 or 20, wherein the ground, densified, embrittled glass particles have an average particle size of less than about 80 microns.

CLAIM 22. The dental restoration of claim 19-21, wherein the polymeric matrix precursor composition comprises at least one acrylate or methacrylate monomer.

CLAIM 23. The dental restoration of claim 19-22, wherein the ground, densified, embrittled glass particles comprise from about 5 % to about 85 % by weight of the total composite composition.

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CLAIM 24. The dental restoration of claim 19-23, wherein the dental composite comprises at least one additional filler material, wherein the filler material is at least one of silica, silicate glass, quartz, barium silicate, strontium silicate, barium borosilicate, borosilicate, lithium silicate, amorphous silica, ammoniated or
5 deammoniated calcium phosphate, alumina, zirconia, tin oxide or titania.

CLAIM 25. The dental restoration of claim 19-24, wherein the elastic modulus is greater than 15 GPa.

CLAIM 26. The dental restoration of claim 19-25, wherein the elastic modulus is between 15 GPa and 22 GPa.

CLAIM 27. The dental restoration of claim 19-26, wherein the dental restoration has a Vicker's hardness of 1250 MPA.

CLAIM 28. The dental restoration of claim 19-27, wherein the restoration has a water sorption of $8.9 \mu\text{g}/\text{mm}^3/\text{week}$.

CLAIM 29. The dental restoration of claim 19-27, wherein the restoration has a depth of cure of at least 5 mm.

CLAIM 30. A cured dental composite comprising:
a cured polymeric material; and
a filler material; wherein the composite has an elastic modulus of greater than approximately 15 GPa.

CLAIM 31. The composite of claim 30 wherein the elastic modulus is between approximately 15 GPa and approximately 22 GPa.

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CLAIM 32 A cured dental composite comprising:
 a cured polymeric material; and
 a filler material; wherein the composite has a Vicker's hardness of 1250 MPA.

CLAIM 33. A cured dental composite comprising:
 a cured polymeric material; and
 a filler material; wherein the composite has a water sorption of 8.9
 $\mu\text{g}/\text{mm}^3/\text{week}$.

CLAIM 34. A cured dental composite comprising:
 a cured polymeric material; and
 a filler material; wherein the composite has a depth of cure of at least 5 mm.

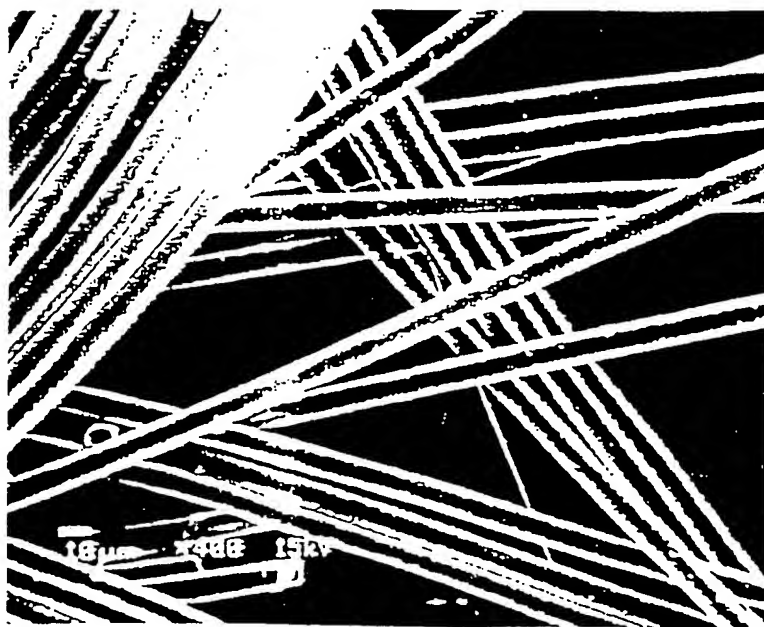


FIG. 1



FIG. 2



FIG. 3A



FIG. 3B



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 6/083	A3	(11) International Publication Number: WO 99/20225 (43) International Publication Date: 29 April 1999 (29.04.99)
(21) International Application Number: PCT/US98/20971 (22) International Filing Date: 6 October 1998 (06.10.98) (30) Priority Data: 08/951,414 16 October 1997 (16.10.97) US 09/092,370 5 June 1998 (05.06.98) US (71) Applicant: JENERIC/PENTRON INCORPORATED [US/US]; 53 North Plains Industrial, Wallingford, CT 06492 (US). (72) Inventors: JIA, Weitao; 6 Valley Street, Wallingford, CT 06492 (US). SCHULMAN, Martin, L.; 620 South Green- briar Drive, Orange, CT 06477 (US). PRASAD, Arun; 249 Redwood Lane, Cheshire, CT 06410 (US). ALPERT, Bruce; 214 Bartlett Drive, Madison, CT 06443 (US). (74) Agent: REIMER, Leah, M.; Fishman, Dionne, Cantor & Colburn, 88 Day Hill Road, Windsor, CT 06095 (US).		(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims</i> <i>and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 19 August 1999 (19.08.99)
(54) Title: DENTAL COMPOSITES COMPRISING GROUND, DENSIFIED, EMBRITTLED GLASS FIBER FILLER		
(57) Abstract		
<p>A composite for a dental restoration is presented comprising ground, densified, embrittled glass fibers together with fillers and a polymeric matrix precursor composition. The ground, densified, embrittled glass fibers are obtained by grinding glass fibers which have been densified and embrittled by heating glass fibers at a temperature substantially below the softening point of the glass fibers, without significant fusion or melting together of the fibers. The composite is particularly useful as a direct filling material, in that it has the feel and workability of an amalgam.</p> <div data-bbox="609 1121 1349 1694" data-label="Image"> </div>		

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/20971

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K6/083

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 017 454 A (MULLER GERD) 12 April 1977 see abstract see column 1, line 11-19 see column 2, line 44-45 see column 4, line 7-14 - line 56-68 see claims 1,4 ---	1,3-6, 12-24
A	DE 43 23 143 C (SCHOTT GLASWERKE) 1 December 1994 see abstract see page 3, line 22-34 --- -/--	1,3,5, 12-15, 19-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

23 June 1999

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MILITKY J ET AL: "ULTIMATE MECHANICAL PROPERTIES OF BASALT FILAMENTS" TEXTILE RESEARCH JOURNAL, vol. 66, no. 4, 1 April 1996, pages 225-229, XP000581413 see abstract see table 1	1,3,12, 13,19,20
A	US 4 392 828 A (EHRNFORD LARS E M) 12 July 1983 see abstract see column 2, line 3-9 see claim 1	1,12,15, 19,22
A	US 4 952 530 A (BROSNAN DENIS A ET AL) 28 August 1990 see abstract see column 1 - column 2 see column 3, line 45-53 see column 4, line 36-38; table 1 see column 5, line 26-40; claim 7	1,3,5, 12-15, 19-22

INTERNATIONAL SEARCH REPORT

...ernational application No.

PCT/US 98/ 20971

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 32-34
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
See FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

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2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
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4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

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- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

Claims Nos.: 32-34

Present claims 32-34 relate to a product defined by reference to the following parameters:

P1: Vicker's hardness of 1250 MPA

P2: water sorption of 8.9 micro g/(mm)³/week ;

P3: depth of cure > 5 mm

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to : Claims 1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/20971

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4017454 A	12-04-1977	DE 2347591 A	03-04-1975
		AT 339523 B	25-10-1977
		AT 692374 A	15-02-1977
		CH 605441 A	29-09-1978
		FR 2244727 A	18-04-1975
		GB 1440172 A	23-06-1976
		JP 998397 C	30-05-1980
		JP 51033117 A	22-03-1976
		JP 54035220 B	01-11-1979
		NL 7412257 A	25-03-1975
		US 3973972 A	10-08-1976
DE 4323143 C	01-12-1994	AU 6340694 A	19-01-1995
		EP 0634373 A	18-01-1995
		JP 7033476 A	03-02-1995
US 4392828 A	12-07-1983	SE 411613 B	21-01-1980
		BE 852458 A	01-07-1977
		CA 1107879 A	25-08-1981
		CH 632408 A	15-10-1982
		DE 2711014 A	29-09-1977
		FR 2344280 A	14-10-1977
		GB 1581067 A	10-12-1980
		NL 7702774 A, B,	20-09-1977
		SE 7603313 A	17-09-1977
		US 4381918 A	03-05-1983
US 4952530 A	28-08-1990	NONE	

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